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# Convergence of Exchange Lattice Summations in Direct-Space Polymer Calculations

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## Abstract

We study various stereoregular polymers (monoatomic (Beryllium chains), diatomic (Hydrogen fluoride chains and polyyne) and polyatomic (polyethylene and polymethineimine)) and monitor the effective convergence of the lattice summations, especially the one corresponding to the exchange contribution. The relations to geometry (bond length alternation), quasi-linear dependencies, basis set and band gap are addressed. Even for extremely conjugated system, the exchange is found to present an exponentially decreasing behavior, rather than a  $1/N^2$  behavior, although convergence can be extremely slow.

Keywords: polymers, crystal-orbital, lattice summations, exchange

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## I. INTRODUCTION

In order to tackle the properties of macromolecules, two strategies may be chosen. In the oligomeric approach, one computes the desired properties on increasingly long oligomers and extrapolates to obtain the polymeric value. For most properties, this convenient molecular approach does not require any new theoretical developments. However, in conjugated systems, the convergence of the properties with respect to chain length may be extremely slow, especially for properties connected to high-order derivatives of the total energy. As a consequence, extremely long oligomers may be necessary in order to obtain accurate extrapolations. In the polymeric approach (or crystal orbital (CO) method), one considers explicitly the translational symmetry of the infinite chain and only a single-shot calculation is necessary to obtain the desired property. This approach was first proposed, independently, by André and Ladik at the end of the sixties and has been reviewed in two monographs more than a decade ago [1, 2]. However, it is only more recently that new developments have been successfully achieved in order to include electron correlation effects [3–6], to analyze excited states [5, 7], to calculate polarizabilities [8, 9], to compute (hyper)polarizabilities [10–14], to correctly determine dipole moments [12] and to evaluate geometrical derivatives of the energy [15–22]. This time gap between initial methodological developments and subsequent works, originates mainly from two factors. On the one hand, polymeric calculations are computationally demanding. On the other hand, numerous difficulties specific to polymeric calculations have been unveiled. In the simple SCF procedure, three main problems have been encountered: 1) To perform a polymeric calculation, one has to perform numerous and complex numerical transformations (in comparison with molecular calculations). Subsequently, when the eigenvalues of the overlap matrix are small (typically, smaller than  $10^{-3}$  a.u.), the inaccuracies on the density matrix tend to propagate rapidly, leading to unphysical results. This is traditionally called a quasi linear-dependency (QLD) problem, to distinguish it from real linear-dependencies (LD) that are found in molecules when the eigenvalues of the metric are smaller than  $10^{-6}$  a.u. As QLD are more frequent with large basis sets and/or when diffuse functions are used, these type of basis sets is generally not used in polymer calculations, although some exceptions can be found, mainly for very alternant systems [23]. Note that the use of relatively small basis sets on extended systems has some theoretical justifications (see, for example Ref. [24]). 2) The integration of the density matrix from

reciprocal to real space may be difficult and requires a specific treatment, especially if a wide range of unit cells has to be used. Indeed, in this case, one has to integrate rapidly oscillating functions. Different procedures have been designed to tackle this phenomena properly [25].

3) The convergence of the lattice summations is problematic. The largest problem arises for the Coulombic effects that are so long-range (LR) that distant unit cells (UC) interact significantly in every polymers. It has been shown by various authors that the different lattice sums corresponding to Coulomb interactions diverge in the expression of the total energy per UC [26–29]. Hopefully, when the reference UC (RUC) has no net charge (i.e. for neutral polymers), all diverging terms cancel each other and a physical energy per UC is obtained [26–29]. Nevertheless, an accurate estimation of the energy requires to take a very large number of UC into account. To limit the number of UC for which the interactions are exactly computed, the multipole expansion technique has been proposed [2, 27, 28]. In this technique, one considers that UC with negligible overlap interact via multipoles rather than via the full Fock operator. For stereoregular polymers, the multipole sums over all cells (up to infinity) can be obtained exactly at a negligible cost once the multipoles of the RUC have been evaluated. This original technique has been extended to the geometrical energy derivatives [20–22]. Together with an analysis of each lattice summations, this has led to the so-called Namur threshold illustrated in Figure 1. In this scheme, all the terms are evaluated completely for  $2N + 1$  cells in the short-range region.  $N$  has to be large enough to allow correct evaluation of the overlap-type and exchange-type integrals. The Coulombic terms are computed exactly up to  $M$  (medium-range region, containing  $2M + 1$  cells; with  $M \geq 2N$ ) and are approximated by Taylor series in the LR region. Teramae has shown that this thresholding technique is the most efficient among the different used in the literature [30]. This success is probably due to the good balance between Coulombic and exchange contributions to the energy that is generally difficult to maintain because they are not treated on an equal footing. For the exchange component, one should consider both integral and density convergence behaviors. For the integrals, it is expected that they decrease as  $1/N$ . The density has been studied theoretically by various authors using quite simple models [31–33]. For polymers with a non-zero gap, the convergence of the density between cell 0 and cell  $\bar{j}$  should be proportional to  $\exp(-\tilde{c}\sqrt{\Delta E}\bar{j})$ , where  $\tilde{c}$  is a proportionality factor and  $\Delta E$  is the band gap [31]. For metallic chains (zero gap), that are generally not treated at the HF level, the convergence pattern of the density is  $1/N$ , giving an overall convergence

of  $1/N^2$ . A convergence accelerating procedure for exchange terms would therefore be an highly desirable feature, especially for small gap systems. Unhappily, a multipole technique adapted to the exchange has only been developed at the simple Pariser-Parr-Pople level [34, 35]. To obtain a fully converged (i.e. exactly up to infinity) exchange term, the Fourier transform method developed by Delhalle, Fripiat and Harris is, at the present, the only available technique, although it is limited, at the moment, to  $s$ -type orbitals [36–38].

In this paper, we use a variety of polymers (polar, non-polar, conjugated or not, ...) in order to assess the behavior of the exchange summations and to determine what are the relations between the basis sets, geometries, quasi-linear dependencies, ... and the actual speed of saturation of the exchange term in Hartree-Fock calculations. To our knowledge, the only similar study has been performed by Suhai in 1980 on polyacetylene using the STO-3G basis set [39]. He found that a  $N=20$  limit was necessary in order to obtain fully converged properties for very conjugated polyacetylene [39].

## II. METHODOLOGY

### A. SCF-LCAO-CO equations

In a polymer, the crystalline orbitals are build as LCAO combinations of real atomic orbitals,  $\chi_\nu$ , given by:

$$\phi_n(k, \vec{r}) = \sum_{\nu=1}^{\omega} C_{\nu,n}(k) \frac{1}{\sqrt{2N+1}} \sum_{\bar{j}=-N}^N e^{ik\bar{j}\bar{a}} \chi_\nu(\vec{r} - \vec{R} - \bar{j}\bar{a}\vec{e}_z) \quad (1)$$

$$= \sum_{\nu=1}^{\omega} C_{\nu,n}(k) \frac{1}{\sqrt{2N+1}} \sum_{\bar{j}=-N}^N e^{ik\bar{j}\bar{a}} \chi_\nu^{\bar{j}} \quad (2)$$

where  $n$  is the band index,  $\omega$  the number of basis functions in the reference unit cell.  $\vec{R}$  is the position of a AO center in the RUC, and  $\vec{e}_z$  a unit vector in the  $z$  direction.  $\bar{a}$  is the unit cell length,  $\bar{j}$  the cell index and  $N$  the number of cells in the short-range region. As can be seen, the LCAO coefficients  $C_{\nu,n}(k)$  depend on the quasi-momentum vector of the

reciprocal space,  $k$ . The corresponding SCF equations are:

$$\sum_{\bar{j}=-N}^{+N} \sum_{\nu}^{\omega} e^{ik\bar{j}\bar{a}} F_{\mu,\nu}^{0,\bar{j}} C_{\nu,n}(k) = \sum_{\bar{j}=-N}^{+N} \sum_{\nu}^{\omega} e^{ik\bar{j}\bar{a}} S_{\mu,\nu}^{0,\bar{j}} C_{\nu,n}(k) \epsilon_n(k) \quad (3)$$

$$\sum_{\nu}^{\omega} F_{\mu,\nu}(k) C_{\nu,n}(k) = \sum_{\nu}^{\omega} S_{\mu,\nu}(k) C_{\nu,n}(k) \epsilon_n(k) \quad (4)$$

where we have defined the  $k$ -space overlap ( $S_{\mu,\nu}(k)$ ) and Fock ( $F_{\mu,\nu}(k)$ ) matrices:

$$S_{\mu,\nu}(k) = \sum_{\bar{j}=-N}^{+N} e^{ik\bar{j}\bar{a}} S_{\mu,\nu}^{0,\bar{j}} = \sum_{\bar{j}=-N}^{+N} e^{ik\bar{j}\bar{a}} \langle \chi_{\mu}^0 | \chi_{\nu}^{\bar{j}} \rangle \quad (5)$$

$$F_{\mu,\nu}(k) = \sum_{\bar{j}=-N}^{+N} e^{ik\bar{j}\bar{a}} F_{\mu,\nu}^{0,\bar{j}} \quad (6)$$

$S_{\mu,\nu}^{0,\bar{j}}$  is the overlap integral between  $\chi_{\mu}$  in the reference unit cell (0) and  $\chi_{\nu}$  in the  $\bar{j}^{\text{th}}$  cell.

$F_{\mu,\nu}^{0,\bar{j}}$  is a term of the real-space Fock matrix, computed as:

$$F_{\mu,\nu}^{0,\bar{j}} = H_{\mu,\nu}^{0,\bar{j}} + \sum_{\bar{l}=-N}^{+N} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}} \sum_{\bar{h}=-\infty}^{+\infty} G_{\mu,\nu,\rho,\sigma}^{0,\bar{j},\bar{h},\bar{h}+\bar{l}} - \frac{1}{2} \sum_{\bar{l}=-N}^{+N} \sum_{\bar{h}=-N}^{+N} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}+\bar{j}-\bar{h}} G_{\mu,\rho,\nu,\sigma}^{0,\bar{h},\bar{j},\bar{j}+\bar{l}} \quad (7)$$

$$= T_{\mu,\nu}^{0,\bar{j}} - V_{\mu,\nu}^{0,\bar{j}} + \sum_{\bar{l}=-N}^{+N} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}} \sum_{\bar{h}=-\infty}^{+\infty} G_{\mu,\nu,\rho,\sigma}^{0,\bar{j},\bar{h},\bar{h}+\bar{l}} - \frac{1}{2} \sum_{\bar{l}=-N}^{+N} \sum_{\bar{h}=-N}^{+N} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}+\bar{j}-\bar{h}} G_{\mu,\rho,\nu,\sigma}^{0,\bar{h},\bar{j},\bar{j}+\bar{l}} \quad (8)$$

$$= -\frac{1}{2} \langle \chi_{\mu}^0 | \nabla^2 | \chi_{\nu}^{\bar{j}} \rangle - \sum_{\bar{h}=-\infty}^{+\infty} \sum_{A=1}^{N_c} \left\langle \chi_{\mu}^0 \left| \frac{Q_A}{|\vec{r} - \vec{R}_A - \bar{h}\bar{a}\vec{e}_z|} \right| \chi_{\nu}^{\bar{j}} \right\rangle + \sum_{\bar{l}=-N}^{+N} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}} \sum_{\bar{h}=-\infty}^{+\infty} G_{\mu,\nu,\rho,\sigma}^{0,\bar{j},\bar{h},\bar{h}+\bar{l}} - \frac{1}{2} \sum_{\bar{l}=-N}^{+N} \sum_{\bar{h}=-M}^{+M} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}+\bar{j}-\bar{h}} G_{\mu,\rho,\nu,\sigma}^{0,\bar{h},\bar{j},\bar{j}+\bar{l}} \quad (9)$$

with  $Q_A$  is the nuclear charge of atom  $A$  and the density matrix,  $P_{\mu,\nu}^{0,\bar{j}}$ , is obtained by an integration over the first Brillouin zone:

$$P_{\mu,\nu}^{0,\bar{j}} = \frac{\bar{a}}{\pi} \int_{-\pi/\bar{a}}^{+\pi/\bar{a}} dk \left[ \sum_{n=1}^{N_{\text{ob}}} C_{\mu,n}(k) C_{\nu,n}^*(k) \right] e^{ik\bar{j}\bar{a}} \quad (10)$$

with  $N_{\text{ob}}$  the number of occupied bands. The two-electron integrals are defined as:

$$G_{\mu,\nu,\rho,\sigma}^{0,\bar{j},\bar{h},\bar{l}} = \int d\vec{r} \int d\vec{r}' \chi_{\mu}^0(\vec{r}) \chi_{\nu}^{\bar{j}}(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \chi_{\rho}^{\bar{h}}(\vec{r}') \chi_{\sigma}^{\bar{l}}(\vec{r}') \quad (11)$$

In this framework, the Hartree-Fock electronic energy is obtained by:

$$E^{\text{elec-SCF}} = \frac{1}{2} \sum_{\bar{j}=-N}^{+N} \sum_{\mu}^{\omega} \sum_{\nu}^{\omega} (H_{\mu,\nu}^{0,\bar{j}} + F_{\mu,\nu}^{0,\bar{j}}) P_{\nu,\mu}^{0,\bar{j}} \quad (12)$$

The exchange contribution of cell  $\bar{j}$  to the SCF energy is therefore given by

$$E^x(\bar{j}) = -\frac{1}{4} \sum_{\mu}^{\omega} \sum_{\nu}^{\omega} P_{\nu,\mu}^{0,\bar{j}} \left( \sum_{\bar{l}=-N}^{+N} \sum_{\bar{h}=-M}^{+M} \sum_{\rho}^{\omega} \sum_{\sigma}^{\omega} P_{\sigma,\rho}^{0,\bar{l}+\bar{j}-\bar{h}} G_{\mu,\rho,\nu,\sigma}^{0,\bar{h},\bar{j},\bar{l}} \right) \quad (13)$$

In Eq. (9), the  $\bar{h}$  summations of the Coulombic terms extend actually to infinity when correct LR terms are included (see introduction). Except for the  $\bar{j}$  sum of exchange, the other summations are directly related to overlap-type terms and, subsequently are guaranteed to converge exponentially. As a consequence, the only open-question is the effective rate of convergence of this  $\bar{j}$  sum.

## B. How to analyze the convergence of the exchange ?

The sole knoweldge of the final SCF energy as a function of  $N$  is a quite poor measure of the saturation rate of the exchange, because the energy is very unsensitive to the quality of the density matrix in a variational procedure. On the other hand, other properties can be very sensitive to exchange convergence [32, 39]. A very recent example can be found in Ref 12:  $N=9$  (i.e. 19 cells) is not sufficient to obtain converged hyperpolarizabilities of conjugated macromolecules. To analyze the exchange convergence, we have computed its contribution to the total SCF energy as a function of  $\bar{j}$  and defined the following parameters:

1.  $N^e(12)$  : the unit cell index such as the exchange contribution to the energy (Eq. (13)) is smaller than  $10^{-12}$  a.u. for all the cells beyond  $|N^e(12)|$ . Such a strict threshold has been chosen in order to ensure a perfect convergence for all properties.
2.  $N^p(6)$  : the unit cell index such as the average density element of  $P_{\nu,\mu}^{0,\bar{j}}$  is smaller than  $10^{-6}$  a.u. for cells beyond  $|N^d(6)|$ . This threshold has been chosen consequently with  $N^e(12)$  :  $10^{-6} = \sqrt{10^{-12}}$ .
3.  $c^e$  : the factor obtained from a least-square fit of the exchange contribution performed with an exponentially decaying function  $[a + b \exp(-c^e \bar{j})]$ . To perform the fits, we consider all the exchange contributions to the energy except those of the cells that are very close to the RUC (from  $\bar{j} = 0$  to  $\bar{j} = 0.2N$ ) or close to the extremities of the short-range region (from  $\bar{j} = 0.9N$  to  $\bar{j} = N$ ) [See later the reason of these limits].
4.  $c^p$  :  $c^e$ , but for the real-space density,  $P_{\nu,\mu}^{0,\bar{j}}$ .

These parameters are compared to the band gap ( $\Delta E = \epsilon_{\text{LUCO}} - \epsilon_{\text{HOCO}}$ ), the smallest exponent of the chosen basis set (SEBS), the number of QLD removed (NQLD) i.e. the number of basis set vectors removed from the SCF procedure, and the smallest eigenvalue of the overlap matrix ( $S_{\mu,\nu}(k)$ ) considered in the calculation after removal of NQLD basis vectors (SESK).

All calculations have been performed with DJpol [40]. The SCF convergence and integral discarding threshold have been set to  $10^{-10}$  a.u. and  $10^{-12}$  a.u., respectively, in order to ensure accurate results.  $M = 2N$  in all calculations, 2 orders of LR correction have been included. The integration method over the first-Brillouin zone has been chosen as a function of  $N$ : 1) for  $30 > N$  : a 48  $k$ -points Gauss-Legendre quadrature 2) for  $50 > N > 30$  : a 256  $k$ -points Clenshaw-Curtiss quadrature 3) for  $N > 50$  : a 501  $k$ -points Filon procedure. This integration scheme guarantees an accuracy of at least  $10^{-10}$  a.u. on the individual  $P_{\mu,\nu}^{0,\bar{j}}$  elements [41]. For the smaller basis sets used, we have checked that the polymeric energies correspond effectively to the extrapolated oligomeric values per unit cell. All calculations have been performed with very large  $N$  (from 15 to 200 depending upon the system, whereas, most polymer calculations tend to use between 3 and 10 [12, 14, 42]).

### III. RESULTS

The chosen systems are sketched in Fig. 2 whereas Table I summarizes the main results. Although there is a wide variety of behaviors (see next sections) some generic conclusions apply to all the system treated.

- The convergence with respect to  $\bar{j}$  of the kinetic or Coulombic terms is always faster than the corresponding exchange saturation even for very alternant polymers (H-F). For all systems treated,  $N=8$  is sufficient to obtain correct (up to  $10^{-14}$  a.u.) kinetic and Coulombic interactions even for basis sets containing diffuse functions. As a consequence, no further treatment of these terms is necessary.
- The convergence rate of the average density or the maximal density element with respect to  $\bar{j}$  are extremely similar, the latter being generally larger by one to two orders of magnitude.



- The decrease of the density and the exchange are exponential in all cases. Indeed, the correlation coefficients of the exponential fits used to determine  $c^e$  and  $c^p$  are always larger than 0.99.
- The square of the average  $P_{\mu,\nu}^{0,\bar{j}}$  value for a given  $\bar{j}$  can be larger or smaller than the exchange contribution to the energy ( $N^e(12)$  can be shorter or longer than  $N^p(6)$  in Table I). Consequently, the knowledge of the density is only an indication but not an accurate measure of the exchange convergence. In other words, the average  $P_{\mu,\nu}^{0,\bar{j}}$  value is not sufficient to ascertain the exchange convergence.
- The sign of the total exchange contribution is of course negative, but it may vary for individual cell. However, in most cases, we found that for cells not close from the center ( $\bar{j}=0$ ), the sign for a given system (polymer, geometry and basis set) tends to be the same for all cells, although it may differ for the positive and negative cell indices. Nevertheless the magnitude of exchange decreases with a similar rate for  $\bar{j} > 0$  and  $\bar{j} < 0$ . Therefore, we consider only the absolute value of exchange contributions and leave the discussion about its sign for further investigations.
- Close to the limit of the short-range region ( $|\bar{j}| \simeq N$ ), the exchange contribution to the energy presents an incorrect behavior, especially for conjugated polymers and when large basis set are used. In general the magnitude of the exchange contribution in the "last" few cells is too large by 1 to 3 orders of magnitude. This overestimation is due to the thresholding technique used: some contributions to cell  $|\bar{j}| \simeq N$  exchange cannot be included, because they would require the density (or Fock) matrix for  $|\bar{j}| > N$  in order to compute it (see Ref. 43 for details). Of course if  $N$  is large enough, this odd behavior is negligible but one has to be a little generous in setting  $N$ , or one has to cut the extreme cell exchange contributions when using Namur's threshold.

## A. Be Chains

In a recent article, Delhalle and coworkers, using a distributed  $s$ -type gaussian function (DSGF) basis set, pointed out, that the exchange contribution should converge extremely slowly in infinite linear Be chains [36]. Despite a large band gap (6.2 eV) they were not able to obtain, using their real-space program, a physical energy whereas, they found possible,

with a Fourier-space program to get a meaningful energy per unit cell (-14.487927 a.u.) [In Ref. 36, the given energy of -14.7489 a.u. is actually a missprint]. In their chosen basis, the *s*-type orbitals that mimic the effective 3-21G *p* orbitals are situated outside but close to the extremities of the reference unit cell. Subsequently the *s*-type functions of neighboring cells overlap substantially (distance < 0.5 Å), although all the eigenvalues of the *k*-space overlap matrix are still larger than  $10^{-3}$  a.u. Moreover, the geometry chosen does not correspond to the global minimum ( $\bar{a} = 2.32$  Å, whereas Be atoms are more stable than any oligomer at this level of theory, see Table II), presumably leading to a quite difficult SCF convergence pattern. Doing the oligomeric calculations with Gaussian94 [44] for chains as large as 54-cell chain, we estimate, by using our usual fitting procedure [45], a polymeric energy of  $-14.48766 \pm 0.00002$  a.u. (see Table II). Using our direct-space code [40] with a large number of cells ( $N=100$ ,  $M=200$ ) and with an unaltered basis set (NDLQ=0), we are able to obtain a converged energy (-14.487684 a.u.) that is actually closer to the extrapolated oligomeric energy than the Fourier-space one. In these chains, the density and exchange contributions are actually following an exponentially decreasing behavior [ $R > 0.99$ ];  $\propto \exp(-0.26\bar{r})$ ,  $\propto \exp(-0.53\bar{r})$ , respectively. For such special case, direct-space calculations are thus completely valid as long as the number of cells taken into account is large enough; in the present case  $N=45$  is necessary to obtain a density converged to  $10^{-6}$  a.u. (see Table I). The  $N$  actually used ( $N=100$ , i.e. 201 cells in the short-range region and 401 cells in the medium-range region) could seem unreasonable but using an efficient thresholding technique during integral computation [41], our cpu-time is only  $\sim 1/6$  of the time used by the current implementation of the Fourier-space method. Of course in the latter, one is guaranteed to obtain converged exchange without having to guess (or modify during the run) the  $N$  value.

## B. H-F Chains

Linear H-F chains ( $d_{\text{H-F}} = 1.78622$  a.u.,  $\bar{a} = 4.67557$  a.u., corresponding to the optimal HF/6-31G geometry [21]) are simple enough to allow the use of basis sets containing up to *f* orbitals. For this alternant system which presents a large gap,  $N=7$  is sufficient to obtain perfectly converged exchange term for any basis set size, as long as no diffuse functions are included. When diffuse functions are added (6-31+G\*, 6-31++G\*), the short-range region

has to be extended (up to 22) and  $c^p$  and  $c^e$  become smaller. As a consequence there is a relationship between SEBS and the speed of saturation, although SEBS is not sufficient to determine this speed. Indeed 6-311G exchange converges faster than 6-31+G\* exchange, although the minimal exponent of the latter is a bit larger. The same kind of relationship could be found with SESK: the smallest SESK correspond to the largest  $N^e(12)$  and  $N^p(6)$ , but again there is no complete continuity in this relationship. As expected, SESK is not only a function of SEBS but also of the basis set size: SESK is divided by  $\sim 10$  by adding polarization functions on the 6-31G basis set although SEBS is unchanged. Similarly cc-pVTZ and 6-311G have the same SEBS but very different SESK. Fig. 3 gives the plot of  $c^p$  as a function of  $\sqrt{\Delta E}$  ( $\Delta E$  is the band gap). If the relationship  $P_{\nu,\mu}^{0,\bar{j}} \propto \exp(-\tilde{c}\sqrt{\Delta E}\bar{j})$  was totally valid, all points of Fig. 3 should belong to the same line. The actual correlation found ( $R = 0.88$ ) is quite poor. Consequently it appears that  $\Delta E$  is a good but not perfect indication of the rate of convergence of the exchange for a given system studied with different types of basis sets.

### C. Polyynes

Polyynes (PY) is a very difficult system to tackle. Indeed, already with a split-valence basis set (6-31G), oligomeric evaluations are limited to short chains [46] and polymeric calculations face QLD/LD troubles [22]. The optimal RHF/6-31G geometry presents an optimal bond length alternation ( $\Delta r = d_{c-c} - d_{c\equiv c}$ ) of 0.1623 Å (see Ref. 22). We have modified  $\Delta r$  by keeping  $\bar{a}$  ( $= d_{c-c} + d_{c\equiv c}$ ) constant and by changing the triple and single bond lengths. In RHF/6-31G polymeric PY calculations, the smallest eigenvalue of the overlap matrix is of the order of  $10^{-7}$  a.u. [22] and the related basis set dimension has to be removed from all calculations: it is a LD [it is not included in NQLD in Table I, because it is an actual LD]. Another small eigenvalue exists ( $\sim 2 \cdot 10^{-4}$  a.u., QLD) and we have monitored the importance of its removal. By reducing the basis set, one eases the calculations:  $N^p(6)$  is divided by a factor ranging from 3 to 8, depending on  $\Delta r$ . This means that one removes the part of the basis set which is related to the long-range conjugation. If the basis set is untouched we have  $N^p(6) > N^e(12)$ , whereas it is the reverse when one dimension is removed. The band gap is almost unaffected by this procedure. Consequently, in some cases, removing a QLD could be a valid procedure: it does not affect the desired property but makes the computation (much)

more simple. When  $\Delta r$  decreases,  $\Delta E$  decreases proportionally to  $\sqrt{\Delta r}$  [ $R > 0.999$ ] for the range of  $\Delta r$  considered here. A smaller  $\Delta r$  corresponds to a better delocalization, larger  $N^e(12)$  and  $N^p(6)$  and smaller  $c^p$  and  $c^e$  coefficients. The  $N^e(12)$  obtained for  $\Delta r = 0.0023$  Å is smaller than for  $\Delta r = 0.0423$  Å because the density is extremely "flat" in the former case. In this case  $c^e$  is a better indicator of exchange saturation speed than  $N^e(12)$ . For very small  $\Delta r$ , one needs extremely large  $N$  to obtain an accurate exchange. As an example for  $\Delta r = 0.0423$  Å,  $N = 120$  is necessary in order to reach the convergence of the average density matrix to  $10^{-6}$  a.u. Fig. 4 sketches the relationship between the  $\sqrt{\Delta r}$  and  $c^p$ . We found a linear relationship with or without including QLD [ $R > 0.99$  in both cases]. So  $\sqrt{\Delta E}$  can take into account geometry modifications although if the basis set is modified one has to use different curves. This corroborates our results on H-F chains. Plots of the logarithm of the exchange contribution as a function of  $\bar{j}$  for the  $\Delta r = 0.0423$  Å and  $0.0023$  Å cases have been drawn (Fig. 5). On this figure it appears that the decay of the exchange is exponential for the two  $\Delta r$  [ $R = 0.999$  and  $0.998$ , respectively]. As a consequence, PY with  $\Delta r = 0.0023$  Å is still not in the metallic regime, although the convergence of the density elements and exchange contributions is extremely slow. Finally, we note that SEBS is a very weak indicator of the exchange saturation rate because it is unsensitive to the geometry. SESK depends on the geometry but not enough to predict the large change in saturation speed noted when  $\Delta r$  is modified.

#### D. Polyethylene and Polymethineimine

A standard geometry has been chosen for polyethylene ( $r_{C-C} = 1.54$  Å,  $r_{C-H} = 1.09$  Å,  $\alpha_{C-C-C} = 109.5$  degrees). For polymethineimine, a polymer similar to polyacetylene where half of the C-H groups are replaced by a N atom, we have used the RHF/6-31G geometry given by Sun [47]. For polyethylene, the prototype of insulators, the convergence with respect to  $\bar{j}$  is fast:  $N = 10$  cells are sufficient to obtain converged density matrix and exchange contribution. For polymethineimine, a  $\pi$ -conjugated chains,  $N = 20$  is required because the speed of saturation ( $c^e$  and  $c^p$ ) is halved. As for H-F, adding of polarization functions does not modify the saturation rate even for polymethineimine.

## IV. CONCLUSIONS

We have studied the convergence of the density matrix elements and exchange contributions to the energy in various polymeric systems. For the non-metallic chains treated here, the convergence is exponential, although for very conjugated polyyne the saturation speed becomes extremely slow. For a given system, the addition of diffuse functions tends to slow the convergence whereas polarization functions do not affect it. The exchange convergence rate is only very loosely related to the smallest eigenvalue of the metric. The square root of the band gap appears as the key parameter to assess convergence for a given system (basis set and NQLD) but becomes quite irrelevant when different basis sets are used. For conjugated systems, large short-range limit ( $N \simeq 20$  to  $40$ ) could be needed in order to obtain perfectly converged properties. For non-conjugated macromolecules one can restrict to  $N \simeq 10$ .

This work highlights the need for developments of schemes able to efficiently accelerate the saturation of the exchange with respect to cell index when studying extremely conjugated polymers.

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# Captions of the figures

Figure 1 : Illustration of the Namur thresholding scheme for polymer calculations.

Figure 2 : Sketch of the different unit cells used.

Figure 3 : Relationship between the square root of the band gap and  $c^p$  for H-F chains treated using different basis sets.

Figure 4 : Relationship between the square root of the band gap and  $c^p$  for polyyne of different bond length alternation. Open (closed) boxes correspond to NQLD=0 (NQLD=1).

Figure 5 : Evolution with cell index of the logarithm of the exchange contribution for polyyne chains (RHF/6-31G,  $\Delta r=0.0423$  Å[circles] and  $\Delta r=0.0023$  Å[triangles]).



TABLE I: Results obtained on the different polymers. See section II.B for the definitions of the different parameters.

Geometry	Basis set	SEBS	$\Delta E$	SESK	NQLD	$N^e(12)$	$N^p(6)$	$c^e$	$c^p$
Be Chains									
$\bar{a}=2.32\text{\AA}$	DGSF	0.0774	0.2273	0.001853	0	36	45	0.53	0.26
H-F Chains									
RHF/6-31G	STO-3G	0.1689	0.9285	0.390845	0	8	9	2.84	1.38
RHF/6-31G	3-21G	0.1832	0.8982	0.102111	0	7	7	3.23	1.56
RHF/6-31G	6-31G	0.1613	0.8917	0.046328	0	7	7	3.40	1.64
RHF/6-31G	6-31G*	0.1613	0.8926	0.004237	0	7	6	3.45	1.66
RHF/6-31G	6-31G**	0.1613	0.8953	0.004201	0	7	6	3.48	1.67
RHF/6-31G	6-31+G*	0.1076	0.8421	0.001553	0	10	12	1.83	0.81
RHF/6-31G	6-31++G*	0.0360	0.7381	0.000629	0	22	16	0.75	0.34
RHF/6-31G	6-311G	0.1027	0.8399	0.008364	0	7	7	2.62	1.22
RHF/6-31G	6-311G*	0.1027	0.8396	0.008224	0	7	7	2.64	1.23
RHF/6-31G	6-311G**	0.1027	0.8413	0.007189	0	7	7	2.76	1.27
RHF/6-31G	cc-pVDZ	0.1220	0.8681	0.033862	0	7	6	3.17	1.40
RHF/6-31G	cc-pVTZ	0.1027	0.8333	0.000834	0	7	6	2.45	1.15
Polyyne									
$\Delta r=0.2423\text{\AA}$	6-31G	0.1687	0.3561	0.000230	0	25	36	0.44	0.20
$\Delta r=0.2023\text{\AA}$	6-31G	0.1687	0.3287	0.000220	0	27	39	0.38	0.18
$\Delta r=0.1623\text{\AA}$	6-31G	0.1687	0.2999	0.000210	0	30	48	0.32	0.15
$\Delta r=0.1223\text{\AA}$	6-31G	0.1687	0.2692	0.000200	0	35	58	0.24	0.11
$\Delta r=0.0823\text{\AA}$	6-31G	0.1687	0.2359	0.000190	0	42	75	0.17	0.08
$\Delta r=0.0423\text{\AA}$	6-31G	0.1687	0.1983	0.000181	0	53	120	0.09	0.04
$\Delta r=0.0023\text{\AA}$	6-31G	0.1687	0.1525	0.000171	0	46	>200	0.04	0.01
$\Delta r=0.2423\text{\AA}$	6-31G	0.1687	0.3559	0.021450	1	15	13	1.56	0.76
$\Delta r=0.2023\text{\AA}$	6-31G	0.1687	0.3285	0.021572	1	18	14	1.41	0.69
$\Delta r=0.1623\text{\AA}$	6-31G	0.1687	0.2997	0.021673	1	18	15	1.24	0.60
$\Delta r=0.1223\text{\AA}$	6-31G	0.1687	0.2690	0.021752	1	21	17	1.09	0.53
$\Delta r=0.0823\text{\AA}$	6-31G	0.1687	0.2357	0.021809	1	24	20	0.93	0.45
$\Delta r=0.0423\text{\AA}$	6-31G	0.1687	0.1982	0.021844	1	29	24	0.70	0.34
$\Delta r=0.0023\text{\AA}$	6-31G	0.1687	0.1524	0.021856	1	38	32	0.52	0.26
Polyethylene									
Standard	STO-3G	0.1689	0.8789	0.197236	0	9	9	2.72	1.31
Standard	3-21G	0.1832	0.6182	0.007290	0	10	9	2.41	1.15
Standard	6-31G	0.1613	0.5838	0.002866	0	9	9	2.45	1.16
Standard	6-31G*	0.1613	0.5886	0.002160	0	10	8	2.46	1.19
Standard	6-31G**	0.1613	0.5880	0.001861	0	9	8	2.48	1.18
Standard	cc-pVDZ	0.1220	0.5472	0.000852	0	9	9	1.67	0.85
Polymethineimine									
RHF/6-31G	STO-3G	0.1689	0.3267	0.197019	0	18	14	1.31	0.64
RHF/6-31G	3-21G	0.1832	0.3027	0.010060	0	18	15	1.24	0.61
RHF/6-31G	6-31G	0.1613	0.3017	0.003883	0	18	14	1.22	0.61
RHF/6-31G	6-31G*	0.1613	0.3244	0.002191	0	17	15	1.27	0.61
RHF/6-31G	6-31G**	0.1613	0.3240	0.002038	0	17	12	1.33	0.65
RHF/6-31G	6-311G	0.1027	0.3026	0.003019	0	18	13	1.23	0.66

TABLE II: Energies per unit cell ( $\Delta E = E(N^{\text{oligo}}) - E(N^{\text{oligo}} - 1)$ ) of Be chains obtained from oligomeric and polymeric calculations using the DSGF basis set of [36]. The extrapolated oligomeric value has been obtained by a specific fitting procedure, see Ref. 45. The Fourier-space value is taken from Ref. 36.

Oligomeric calculations	
$N^{\text{oligo}}$	SCF energies
1	-14.488962230
10	-14.478056633
20	-14.485781262
30	-14.487359887
40	-14.487576024
50	-14.487626158
51	-14.487628916
52	-14.487631457
53	-14.487633808
54	-14.487635988
Extrapolation : $\infty$ -14.48766 $\pm$ 0.00002	
Polymer calculations	
Direct-space	-14.487684
Fourier-space	-14.487927 (Ref. 36)